SYNTHESIS OF POLY-(ALKYLENE GLYCOL DITHIOPHOSPHATE)S AND SOME OF THEIR ADDITION REACTIONS*

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WE HAVE previously reported the production of poly-(alkylene glycol dithiophosphate)s by the polyesterification of diethyl dithiophosphate with various glycols [1]. Poly-(alkylene glycol dithiophosphate)s have proved to be extremely interesting compounds, capable od adding to the double bonds of unsaturated compounds, of salt formation, and so on. In the present work, we have studied the influence of various experimental conditions—reaction time, temperature, and pressure—on the molecular weight of the polymers formed.

The subjects of the investigation were 1,4-butylene glycol, diethyleneglycol, and ethylene glycol, and diethyl dithiophosphate. The reaction time affected the polymerization coefficient of the polyester from 1,4-butylene glycol and diethyl dithiophosphate in the following way:

Reaction time, hours	2	2·5	3	4
Molecular weight of the polyester	682	880	1240	polymer insoluble in dioxane

The reactions were carried out with equimolecular ratios of the reactants at a residual pressure of 40 mm and a temperature gradually changing from 80 to 120°. The molecular weights of the polyesters were determined cryoscopically. The influnce of the reaction temperature on the molecular weights of the polyesters formed from diethyleneglycol and diethyl dithiophosphate at a constant reaction time (3 hours) and a residual pressure of 40 mm was found: the numerical data are given below:

Range of polycondensation temperatures, °C	80–100	80–110	80–120	80–130	80–140
Mol. wt. of the polyester	1021	1077	1091	1138	1268

The influence of the change in the residual pressure on the molecular weight of the polyester at a constant reaction time (1 hour), a temperature of 80–120°, and a ratio of ethylene glycol to diethyl dithiophosphate of 1·2 : 1 was studied; the corresponding numerical results are given below:

Residual pressure, mm	100	80	60	40
Mol. wt. of the polyester	527	640	704	769

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